

## Module: I

What is Metal?

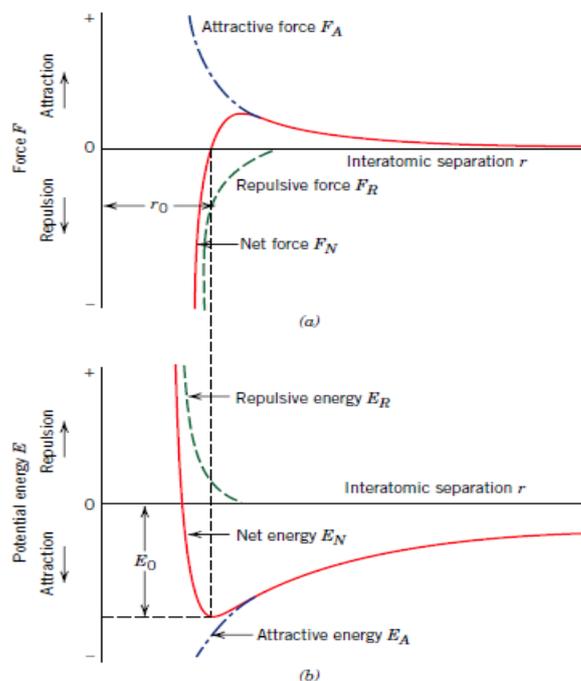
Chemist: A metal if its oxide dissolved in water and gives an alkaline solution.

Physics: Good electrical conductivity of metal, which decreases with the increase of temperature

Metallurgist: Metal possess reasonable plasticity and the metallic properties can be changed for structural and other useful applications.

Bonding forces and Energy:

An understanding of many of the physical properties of materials is enhanced by a knowledge of the interatomic forces that bind the atoms together. Perhaps the principles of atomic bonding are best illustrated by considering how two isolated atoms interact as they are brought close together from an infinite separation. At large distances, interactions are negligible, because the atoms are too far apart to have an influence on each other; however, at small separation distances, each atom exerts forces on the other. These forces are of two types, attractive ( $F_A$ ) and repulsive ( $F_R$ ), and the magnitude of each depends on the separation or interatomic distance ( $r$ ); Figure 1a is a schematic plot of  $F_A$  and  $F_R$  versus  $r$ . The origin of an attractive force  $F_A$  depends on the particular type of bonding that exists between the two atoms, as discussed shortly. Repulsive forces arise from interactions between the negatively charged electron clouds for the two atoms and are important only at small values of  $r$  as the outer electron shells of the two atoms begin to overlap (Figure 1a).



**Figure 1** (a) The dependence of repulsive, attractive, and net forces on interatomic separation for two isolated atoms.

(b) The dependence of repulsive, attractive, and net potential energies on interatomic separation for two isolated atoms

The net force  $F_N$  between the two atoms is just the sum of both attractive and repulsive components; that is,

$$F_N = F_A + F_R$$

which is also a function of the interatomic separation, as also plotted in Figure 1a. When  $F_A$  and  $F_R$  balance, or become equal, there is no net force; that is,

$$0 = F_A + F_R$$

and a state of equilibrium exists. The centers of the two atoms will remain separated by the equilibrium spacing  $r_0$ , as indicated in Figure 2.8a. For many atoms,  $r_0$  is approximately 0.3 nm. Once in this position, any attempt to move the two atoms farther apart will be counteracted by the attractive force, while pushing them closer

together will be resisted by the increasing repulsive force. Sometimes it is more convenient to work with the potential energies between two atoms instead of forces. Mathematically, energy ( $E$ ) and force ( $F$ ) are related as

$$E = \int F dr$$

$$E_N = \int_{\infty}^r F_N dr$$

$$= \int_{\infty}^r F_A dr + \int_{\infty}^r F_R dr$$

$$= E_A + E_R$$

in which  $E_N$ ,  $E_A$ , and  $E_R$  are respectively the net, attractive, and repulsive energies for two isolated and adjacent atoms.

Figure 1b plots attractive, repulsive, and net potential energies as a function of interatomic separation for two atoms. From Equation 2.7, the net curve is the sum of the attractive and repulsive curves. The minimum in the net energy curve corresponds to the equilibrium spacing,  $r_0$ . Furthermore, the **bonding energy** for these two atoms,  $E_0$ , corresponds to the energy at this minimum point (also shown in Figure 1b); it represents the energy that would be required to separate these two atoms to an infinite separation.

Although the preceding treatment deals with an ideal situation involving only two atoms, a similar yet more complex condition exists for solid materials because force and energy interactions among many atoms must be considered. Nevertheless, a bonding energy, analogous to  $E_0$  above, may be associated with each atom. The magnitude of this bonding energy and the shape of the energy-versus-interatomic separation curve vary from material to material, and they both depend on the type of atomic bonding. Furthermore, a number of material properties depend on  $E_0$ , the curve shape, and bonding type. For example, materials having large bonding energies typically also have high melting temperatures; at room temperature, solid substances are formed for large bonding energies, whereas for small energies the gaseous state is favored; liquids prevail when the energies are of intermediate magnitude. In addition, as discussed in Section 6.3, the mechanical stiffness (or modulus of elasticity) of a

material is dependent on the shape of its force-versus-interatomic separation curve (Figure 6.7). The slope for a relatively stiff material at the  $r = r_0$  position on the curve will be quite steep; slopes

are shallower for more flexible materials. Furthermore, how much a material expands upon heating or contracts upon cooling (that is, its linear coefficient of thermal expansion) is related to the shape of its  $E_0$ -versus- $r_0$  curve (see Section 19.3). A deep and narrow “trough,” which typically occurs for materials having large bonding energies, normally correlates with a low coefficient of thermal expansion and relatively small dimensional alterations for changes in temperature

Three different types of **primary** or chemical **bond** are found in solids—ionic, covalent, and metallic. For each type, the bonding necessarily involves the valence electrons; furthermore, the nature of the bond depends on the electron structures of the constituent atoms. In general, each of these three types of bonding arises from the tendency of the atoms to assume stable electron structures, like those of the inert gases, by completely filling the outermost electron shell.

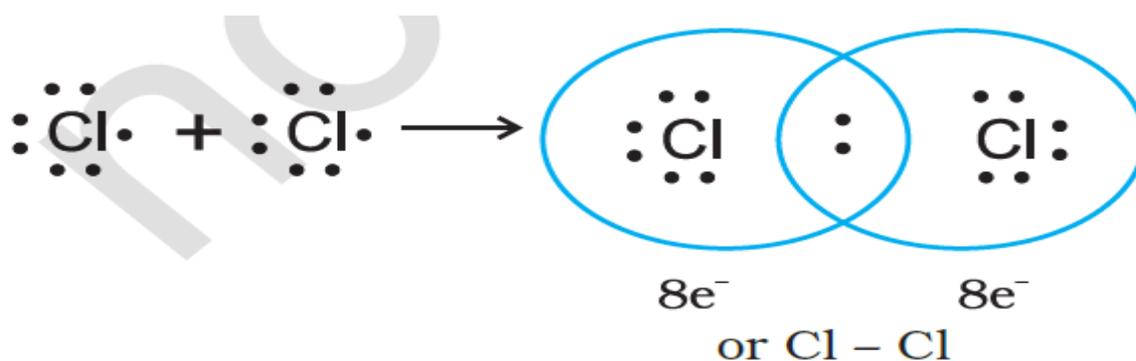
Secondary or physical forces and energies are also found in many solid materials; they are weaker than the primary ones, but nonetheless influence the physical properties of some materials. The sections that follow explain the several kinds of primary and secondary interatomic bonds.

Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously, there must be some force which holds these constituent atoms together in the molecules. The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond

Chemical compounds are formed by the bonding of two or more atoms. A stable bonding forms when the total energy of the combination has lower energy than the separated atoms. The bound state implies a net attractive force between the atoms called a chemical bond. Chemical bonds are classified in to many types.

Octet rule : Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as octet rule

Co-valent bond: Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term covalent bond. The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule,  $\text{Cl}_2$ . The Cl atom with electronic configuration,  $[\text{Ne}]3s^2 3p^5$ , is one electron short of the argon configuration. The formation of the  $\text{Cl}_2$  molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon). The dots represent electrons. Such structures are referred to as Lewis dot structures.



### *Covalent bond between two Cl atoms*

when two atoms share one electron pair they are said to be joined by a single covalent bond.

**Ionic Bond:** From the Kössel and Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon: • The ease of formation of the positive and negative ions from the respective neutral atoms; • The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound. The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom. Ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy

A qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state.

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol<sup>-1</sup>. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na<sup>+</sup> (g) and one mole of Cl<sup>-</sup> (g) to an infinite distance. This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included

**Vander waals Bond:** It is a secondary bonding. It joins (bonds) molecules or group of atoms by weak weak electrostatic attraction, but the atom within the molecule or group of atoms are bonded by strong co-valent or ionic bond. For example, heating water to its boiling point (100 °C) breaks the vander waals bonds in between the water molecules, and changes water to steam. But heating to much higher temperature is needed to break the covalent bonds joining oxygen and hydrogen atoms of each water molecule.

**Metallic Bonding:** The metallic bond can be described in a similar way as the covalent bond. The main difference between these two bond types is that the ionization energy for electrons occupying the outer orbitals of the metallic elements is much smaller. In typical metals, like the alkali metals, these outer orbitals are spherical s-orbitals allowing overlapping with up to 12 further s-orbitals of the surrounding atoms. Thus, the well-defined electron localization in bonds connecting pairs of atoms with each other loses its meaning. Quantum-mechanical calculations show that in large agglomerations of metal atoms the delocalized bonding electrons occupy lower energy levels than in the free atoms; this would not be true for isolated “metal molecules”. The metallic bond in typical metals is non-directional, favoring structures corresponding to closest packings of spheres. With increasing localization of valence electrons,

covalent interactions cause deviations from spherically symmetric bonding, leading to more complicated structures.

The lack of oppositely charged ions in the metallic structure and the lack of sufficient valence electrons to form a true covalent bond necessitate the sharing of valence electrons by more than two atoms. Each of the atoms of the metal contributes its valence electrons to the formation of a negative electron "cloud." These electrons are not associated with a particular ion but are free to move among the positive metallic ions in definite energy levels. The metallic ions are held together by virtue of their mutual attraction for the negative electron cloud. The metallic bond may be thought of as an extension of the covalent bond to a large number of atoms.

### Crystal structure

Since atoms tend to assume relatively fixed positions, this gives rise to the formation of crystals in the solid state. The atoms oscillate about fixed locations and are in dynamic equilibrium rather than statically fixed. The three-dimensional network of imaginary lines connecting the atoms is called the space lattice, while the smallest unit having the full symmetry of the crystal is called the *unit cell*. The specific unit cell for each metal is defined by its parameters (Fig. 2), which are the edges of the unit cell  $a$ ,  $b$ ,  $c$  and the angles  $\alpha$  (between  $b$  and  $c$ ),  $\beta$  (between  $a$  and  $c$ ), and  $\gamma$  (between  $a$  and  $b$ ). There are only 14 possible types of space lattices, and they fall into seven crystal systems listed in table.1.

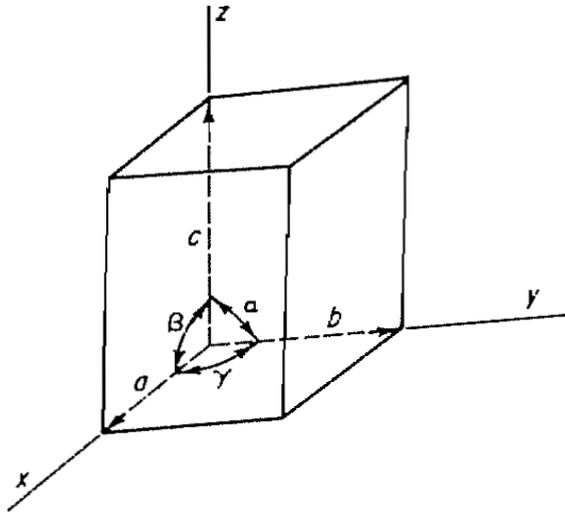


Fig.2. Space lattice illustrating lattice parameters

Table 1. Relation between lattice parameters for seven crystal systems

Sl No	System	Axes	Axial angles	Bravis lattices
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	S, B, F
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	S, B
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	S, Base, B, F
4	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	S
5	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	S
6	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	S, Base
7	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	S

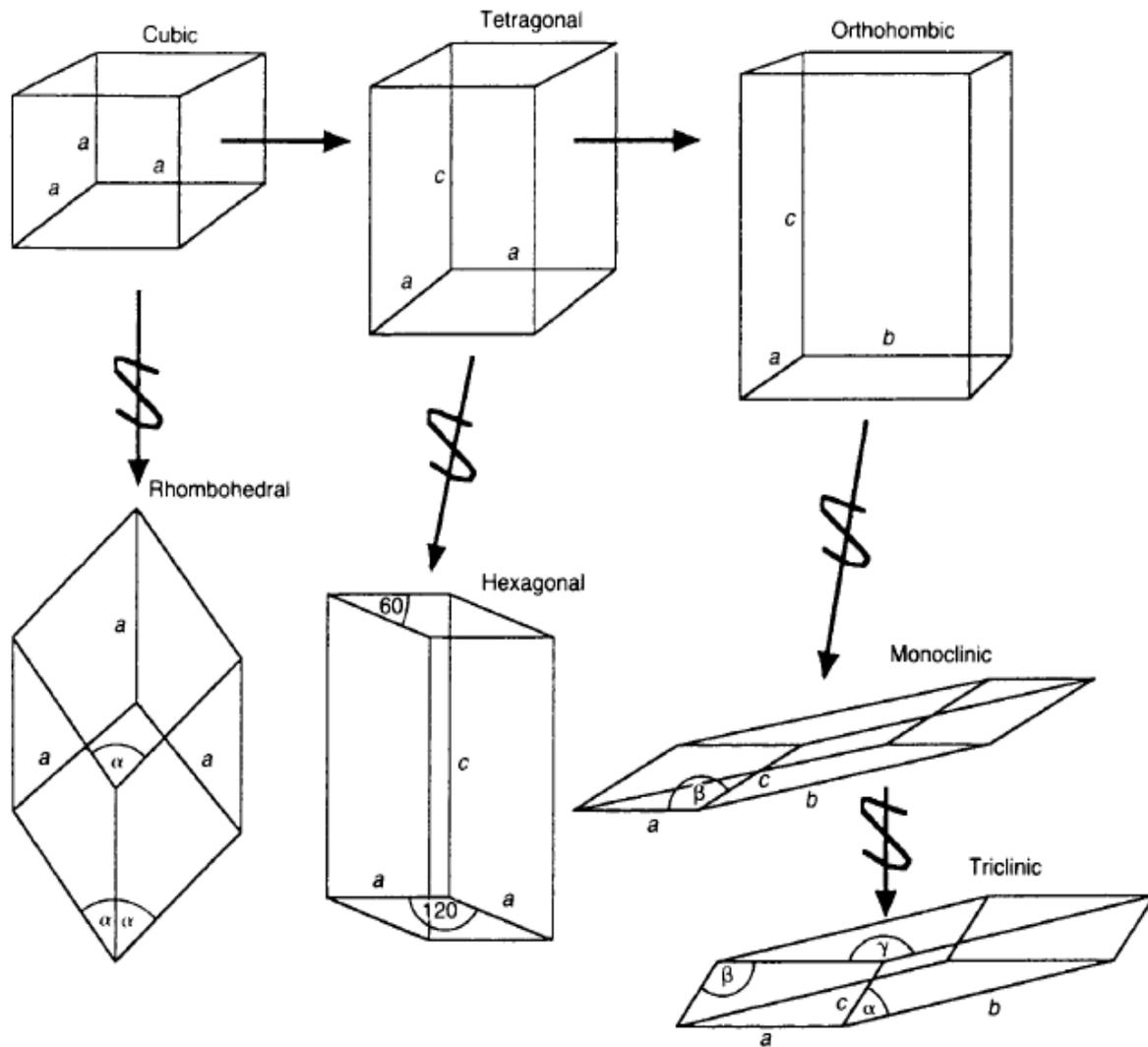


Fig.3. Seven crystal systems

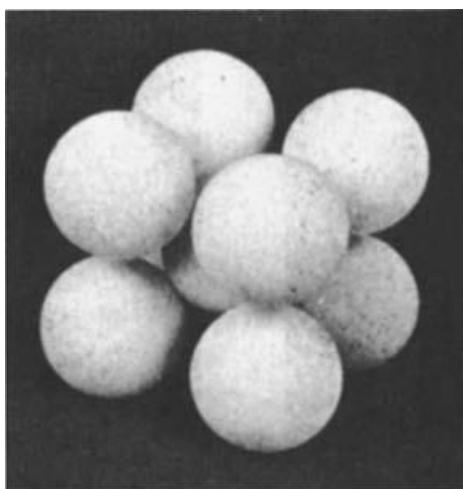


Fig.4. Hard-ball model of the body-centered cubic unit cell

If the atoms are represented as spheres, the center atom touches each corner atom but these do not touch each other. Since each corner atom is shared by eight adjoining cubes and the atom in the center cannot be shared by any other cube the unit cell of the b.c.c. structure contains: (Effective no of atoms per unitcell):

8 atoms at the corners  $\times 1/8 = 1$  atom

1 center atom = 1 atom

Total = 2 atoms

Co-ordination No (The coordination number of a crystal structure equals the number of nearest neighbors

that an atom possesses in the lattice.) =  $Z = 8$

Atomic radii:  $r = \frac{\sqrt{3}a}{4}$

Atomic Packing Fraction (APF) = Volume of the effective number of atoms present in a unit cell / volume of the unit cell = 0.68 or 68%

Face Centered Cubic (FCC)

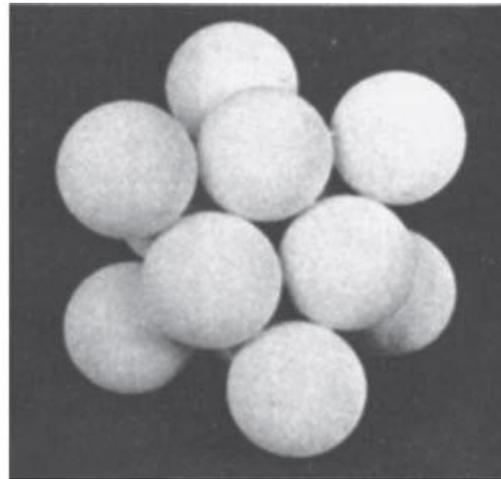
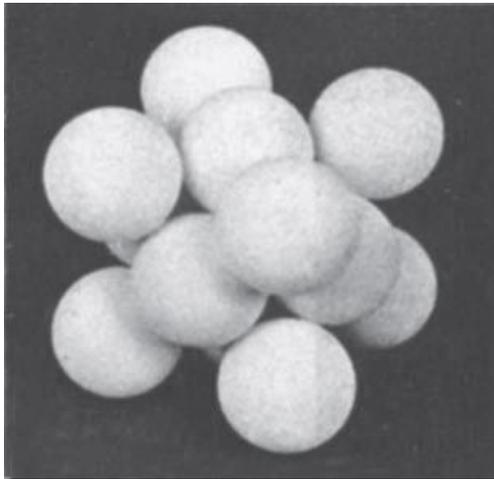


Fig.5. (A) Face-centered cubic unit cell (hard-ball model). (B) Same cell with a corner atom removed to show an octahedral plane.

Effective number of atoms per unit cell =  $1/8 \times 8 + 1/2 \times 6 = 4$

Atomic radius:  $r = a / 2\sqrt{2}$

APF = 0.74 Or 74 %

Co-ordination no =  $Z = 12$

Stacking Sequence: ABCABCABC.....

Hexagonal Closed Packed Structure (HCP)

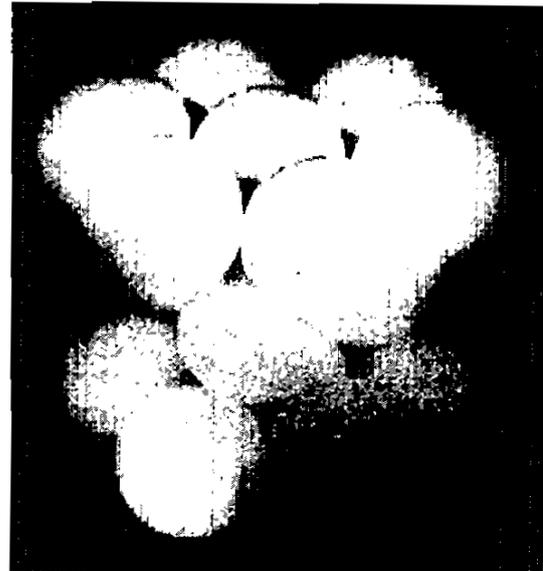
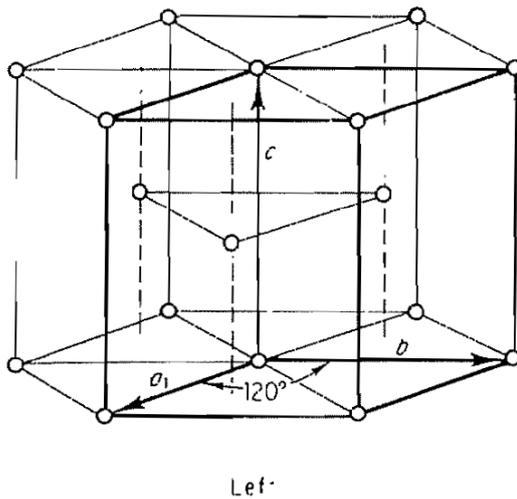


Fig.6. HCP Structure

Effective number of atoms per unit cell =  $12 \times 1/6 + 2 \times 1/2 + 3 = 6$

Atomic radius:  $r = a / 2$

APF = 0.74 Or 74 %

Co-ordination no =  $Z = 12$

Stacking Sequence: ABABAB.....

### Miller Indices

Miller indices are used to specify **directions** and **planes**. These directions and planes could be in **lattices** or in **crystals**

How to Calculate miller indices of a plane?

Step 1: Take the intercept in X Y and Z direction or in a b and c lattice direction. For example, the intercepts are 2, 3 and 1 respectively.

Step 2: Take the reciprocals of the intercepts. That is  $1/2$  ,  $1/3$  and  $1/1$

Step 3: Change the reciprocals into smallest integers having the same ratio. That is 3, 2 and 6

Step 4: Enclose in parenthesis. That is (3 2 6)

Unknown direction  $\rightarrow [u \ v \ w]$

Family of directions  $\rightarrow \langle u \ v \ w \rangle$

Unknown plane  $\rightarrow (h \ k \ l)$

Family of planes  $\rightarrow \{h \ k \ l\}$

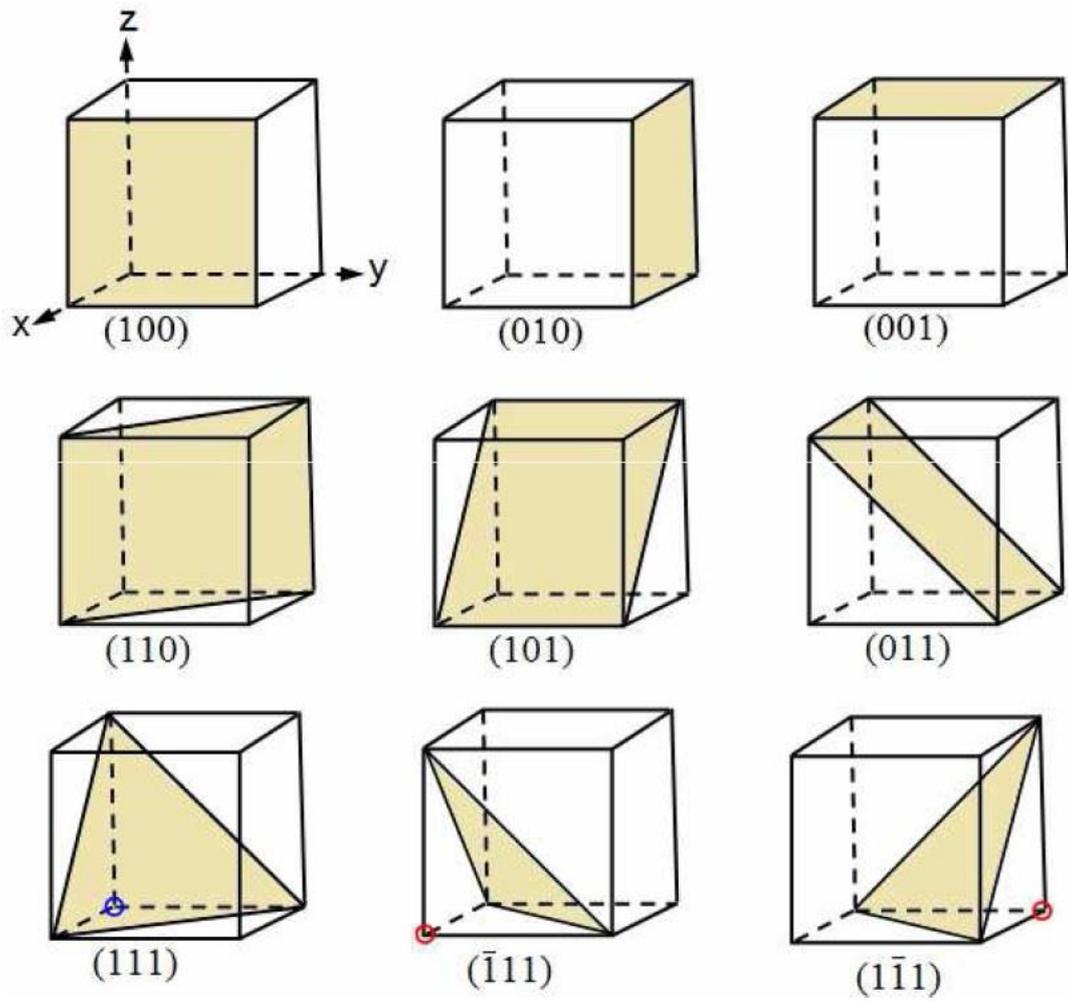


Fig.7. Crystallographic planes

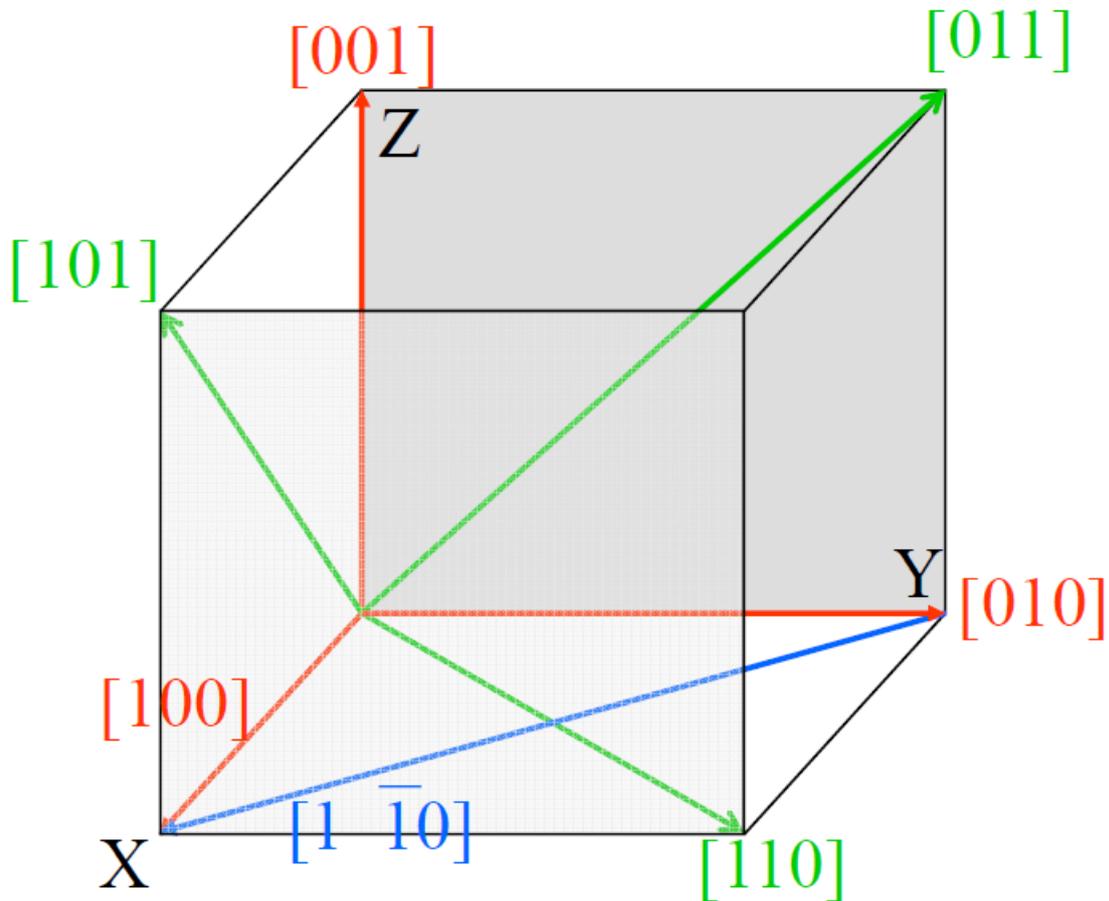


Fig.8. Crystallographic directions

#### Miller Indices for Hexagonal Crystals

Directions and planes in hexagonal lattices and crystals are designated by the 4-index Miller-Bravais notation

In the four index notation: the first three indices are a symmetrically related set on the basal plane

The third index is a *redundant one* (which can be derived from the first two) and is introduced to make sure that members of a family of directions or planes have a set of numbers which are identical

The fourth index represents the 'c' axis (perpendicular to the basal plane)

Let us now determine the Miller indices of several important close-packed hexagonal lattice planes. The uppermost surface of the unit cell in Fig. 9 corresponds to the basal plane of the crystal. Since it is parallel to the axes  $a_1$ ,  $a_2$ , and  $a_3$ , it must intercept them at infinity. Its  $c$  axis intercept, however, is equal to 1. The reciprocals of these intercepts are  $1/\infty, 1/\infty, 1/\infty, 1/1$ . The Miller indices of the basal plane are, therefore, (0001). The six vertical surfaces of the unit cell are known as *prism planes* of Type 1. Consider now the prism plane that forms the front face of the cell, which has intercepts as follows:  $a_1$  at 1,  $a_2$  at infinity,  $a_3$  at -1, and  $c$  at infinity. Its Miller indices are, therefore, (10 0). Another important type of plane in the hexagonal lattice is shown in Fig. 9. The intercepts are  $a_1$  at 1,  $a_2$  at infinity,  $a_3$  at -1, and  $c$  at 1/2 and the Miller indices are accordingly (1012).

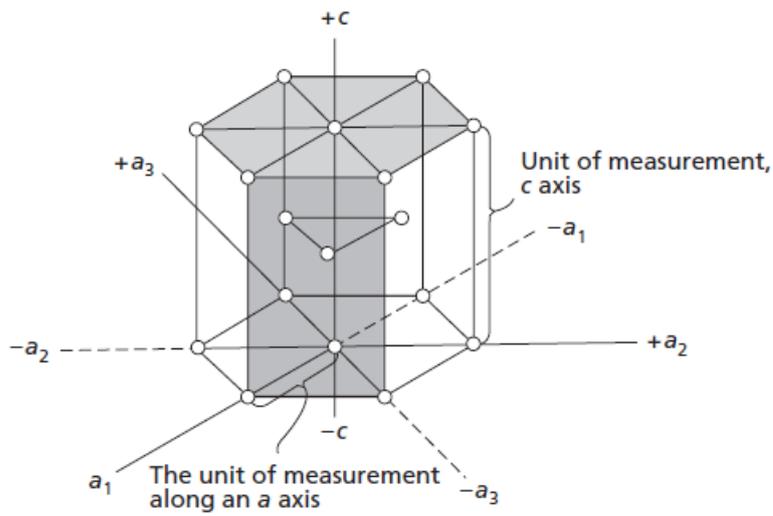


Fig.9. Hexagonal Close Packed Structure

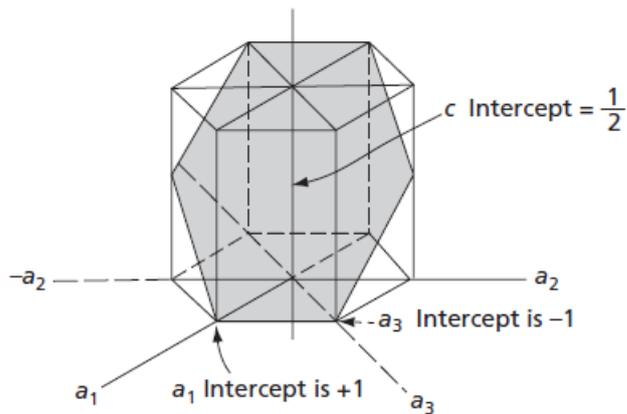


Fig.10. Hexagonal Close Packed Structure

Miller indices of directions are also expressed in terms of four digits. In writing direction indices, the third digit must always equal the negative sum of the first two digits. Thus, if the first two digits are 3 and 1, the third must be  $\bar{4}$ , that is,  $[3\ 1\ \bar{4}\ 0]$ .

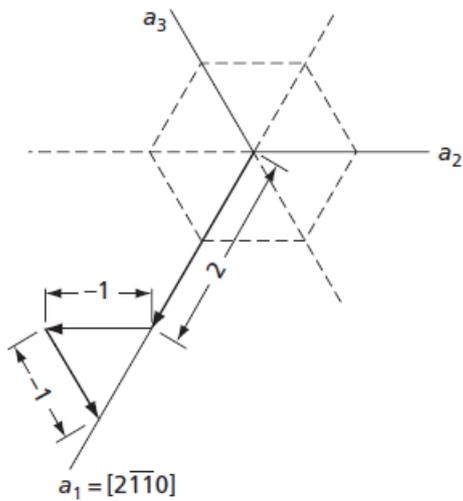


Fig.11.

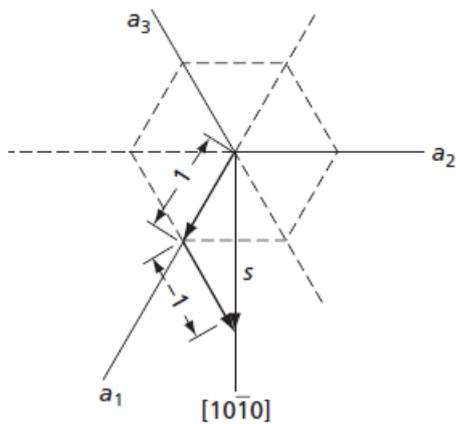


Fig.12.

## THE STEREOGRAPHIC PROJECTION

The stereographic projection is a useful metallurgical tool, for it permits the mapping in two dimensions of crystallographic planes and directions in a convenient and straightforward manner. The real value of the method is attained when it is possible to visualize crystallographic features directly in terms of their stereographic projections. The purpose of this section is to concentrate on the geometrical correspondence between crystallographic planes and directions and their stereographic projections. In each case, a sketch of a certain crystallographic feature, in terms of its location in the unit cell, is compared with its corresponding stereographic projection.

Several simple examples will be considered, but before this is done, attention will be called to several pertinent facts. The stereographic projection is a two-dimensional drawing of three-dimensional data. The geometry of all crystallographic planes and directions is accordingly reduced by one dimension. Planes are plotted as great circle lines, and directions are plotted as points. Also, the normal to a plane completely

describes the orientation of a plane.

As our first example, consider several of the more important planes of a cubic lattice: specifically the (100), (110), and (111) planes. All three planes are treated in the three parts of Fig. 12. Notice that the stereographic projection of each plane can be represented either by a great circle or by a point showing the direction in space that is normal to the plane.

Many crystallographic problems can be solved by considering the stereographic projections of planes and directions in a single hemisphere, that is, normally the one in front of the plane of the paper. The three examples given in Fig. 12 have all been plotted in this manner. If the need arises, the stereographic projections in the rear hemisphere can also be plotted in the same diagram. However, it is necessary that the projections in the two hemispheres be distinguishable from each other. This may be accomplished if the stereographic projections of planes and directions in the forward hemisphere are drawn as solid lines and dots, respectively, while those in the rear hemisphere are plotted as dotted lines and circled dots, respectively. As an illustration, consider Fig. 1.21, in which the projections in both hemispheres of a single plane are shown. The (120) plane of a cubic lattice is used in this example

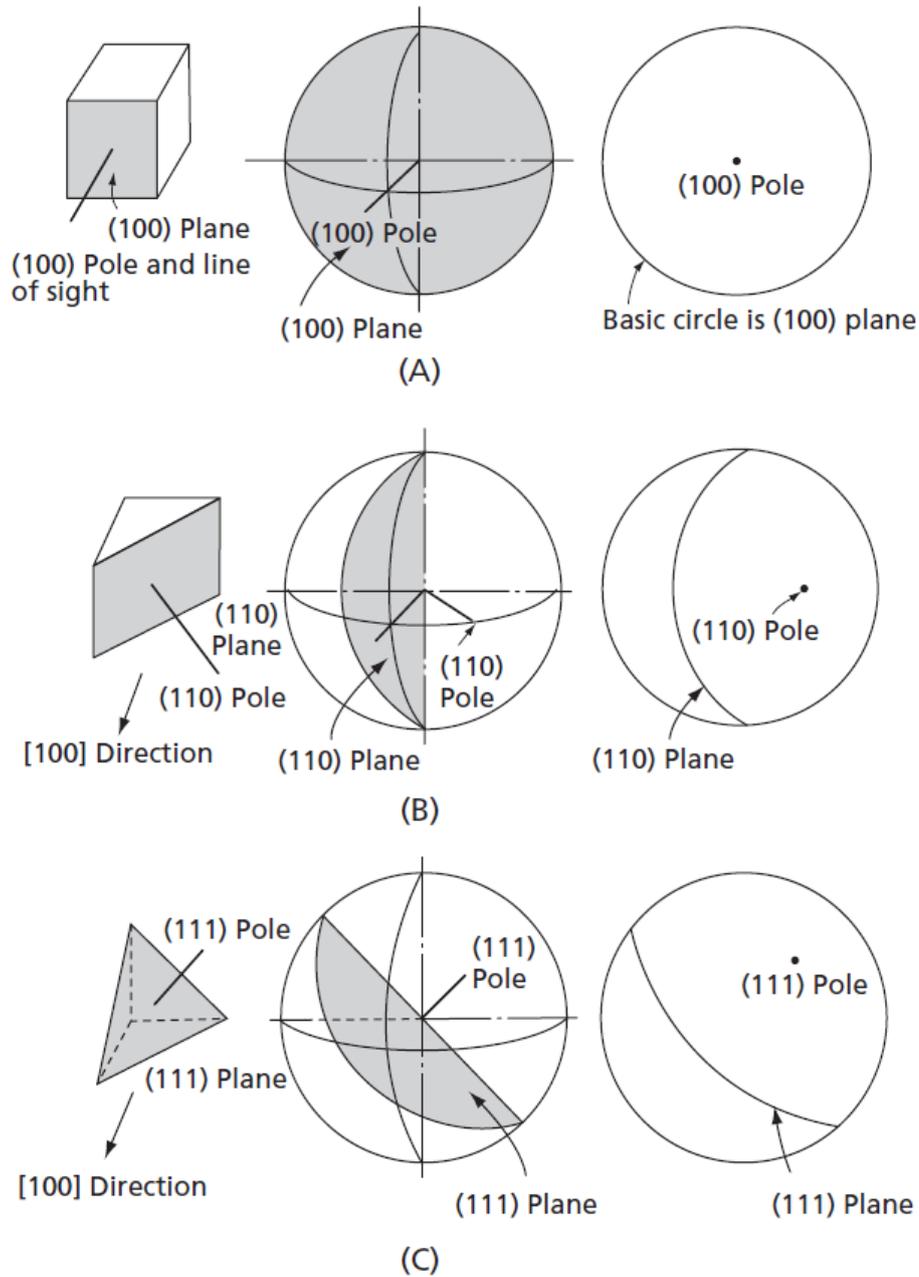


FIG. 13. Stereographic projections of several important planes of a cubic crystal. (A) The (100) plane, line of sight along the [100] direction. (B) The (110) plane, line of sight along the [100] direction. (C) The (111) plane, line of sight along the [100] direction

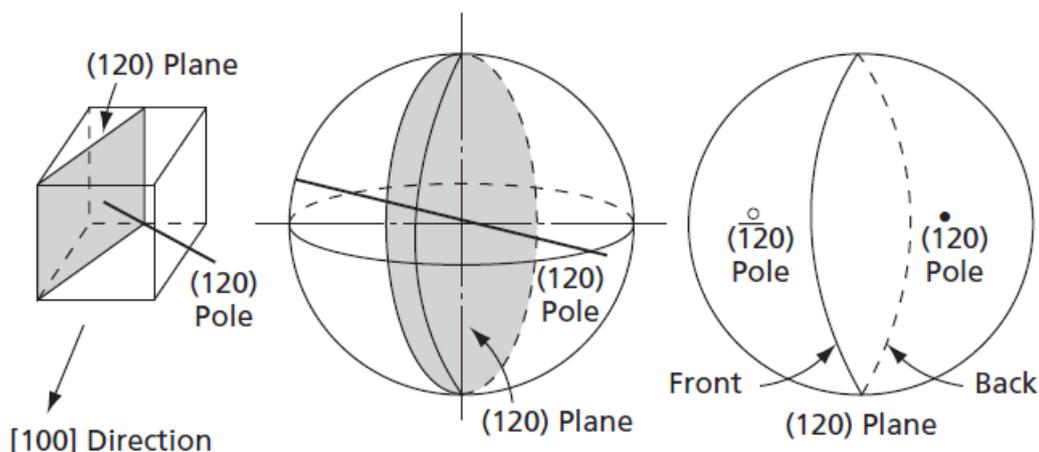
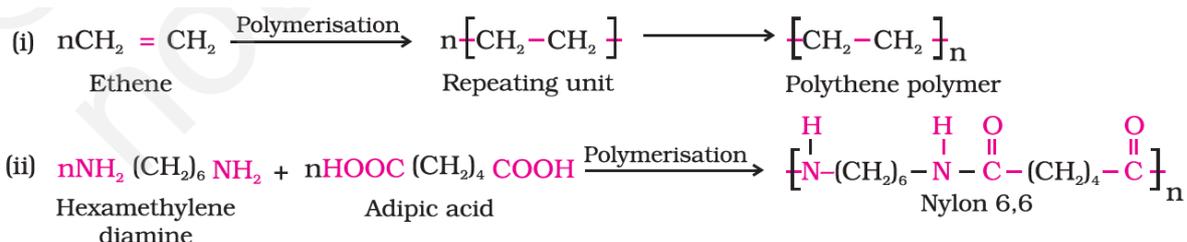


FIG. 14. Cubic system, the (120) plane, showing the stereographic projections from both hemispheres, line of sight the [100] direction

## Polymer

The word 'polymer' is coined from two Greek words: poly means many and mer means unit or part. The term polymer is defined as very large molecules having high molecular mass (10<sup>3</sup>-10<sup>7</sup>u). These are also referred to as macromolecules, which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerisation. The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6, 6 are examples of two different types of polymerisation reactions

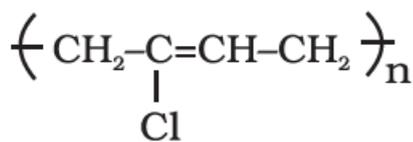


Classification of polymer Based on Molecular Forces: A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.

### 1. Elastomers

These are rubber – like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak

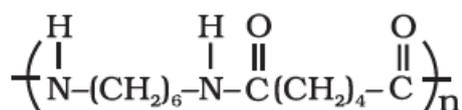
binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.



Neoprene

## 2. Fibers

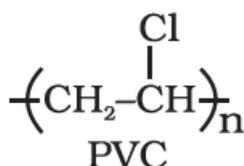
Fibers are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.



Nylon 6,6

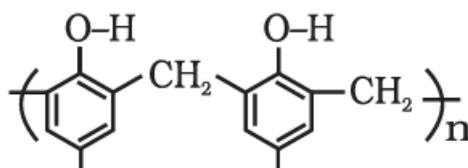
## 3. Thermoplastic polymers

These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.



## 4. Thermosetting polymers

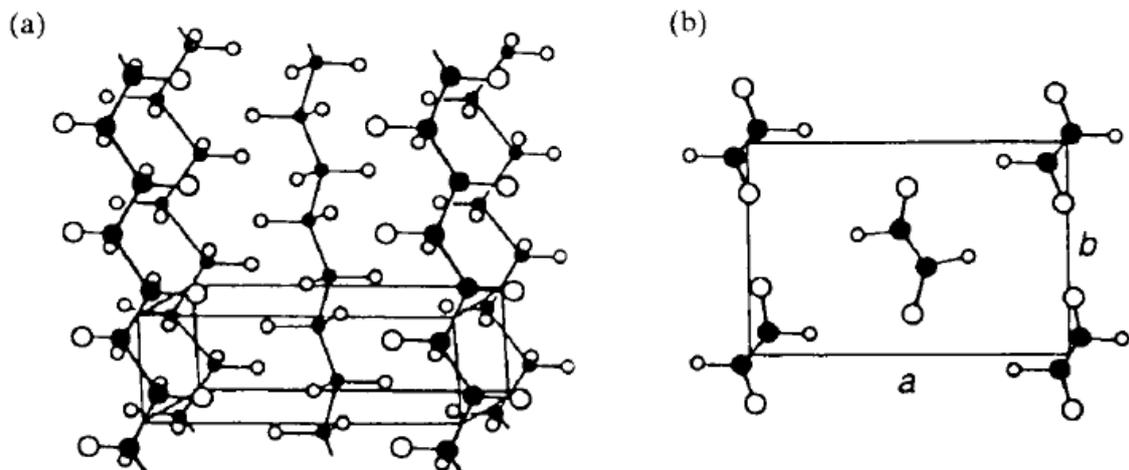
These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc



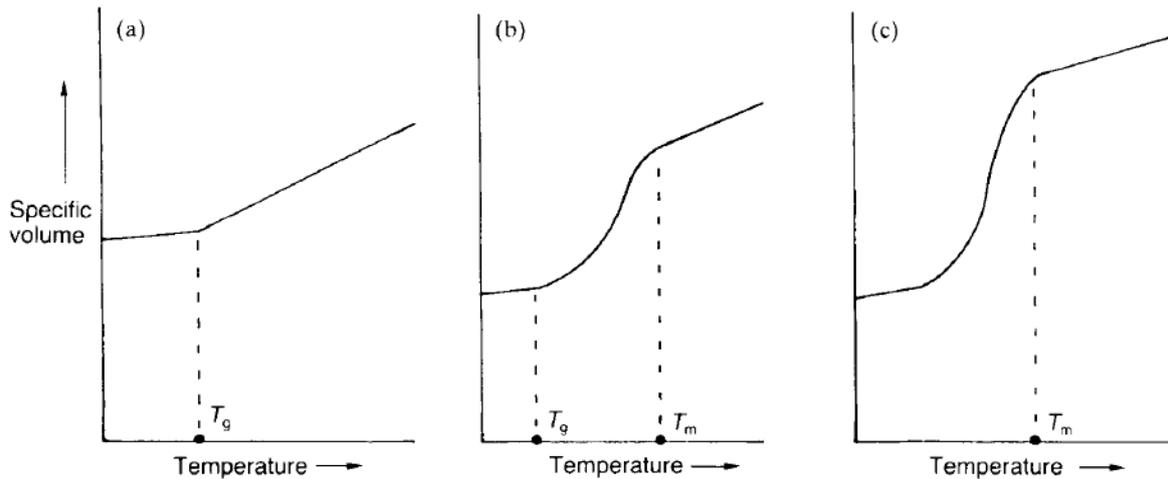
Bakelite

## Crystallinity in polymers

Thermoplastic polymers are essentially disordered (non-crystalline) structures in which chain molecules of various lengths form a tangled mass. This image is quite appropriate for some polymers e.g. polystyrene and polymethyl methacrylate (*Perspex*). However, as indicated in the case of stressed elastomers it is possible for chain molecules to form regions in which repeat units are aligned in close-packed, ordered arrays. Crystalline regions in polymers are generally lamellar in form and often small, with their smallest dimension in the order of 10–20 nm. Inevitably, because of the complexity of the molecules, crystallized regions are associated with amorphous regions and defects. However, the degree of crystallinity attainable can approach 80–85% by volume of the structure. Thus, in polyethylene (PE), a simple ‘linear’ thermoplastic that has been the subject of much investigation, crystalline regions nucleate and grow extremely rapidly during polymerization, their formation being virtually unpreventable. Values of 50% and 80%, respectively, are quoted for the crystallinity of its low- and high-density forms, LDPE and HDPE. A medium-density form provides an appropriate balance of strength and flexibility and has been used for the yellow distribution pipes which convey natural gas in the UK. Crystalline regions are close packed and act as barriers to the diffusion of gases and small molecules. This impermeability favours the use of LDPE for food wrappings. HDPE, being even more crystalline, has a lower permeability to gases and vapours than LDPE.



**Figure 15** Crystal structure of orthorhombic polyethylene. (a) General view of unit cell. (b) Projection of unit cell parallel to the chain direction ● Carbon atoms, ○ Hydrogen atoms



**Figure 16.** Specific volume versus temperature plots for (a) 100% amorphous polymer, (b) partially-crystalline polymer, (c) 100% crystalline polymer

### Pure Metal

Table 2: Crystal structure of some metal at room temperature

<i>Element</i>	<i>Crystal structure</i>	<i>Closest interatomic distance (nm)</i>	<i>Element</i>	<i>Crystal structure</i>	<i>Closest interatomic distance (nm)</i>
Aluminium	fcc	0.286	Platinum	fcc	0.277
Beryllium	cph ( $c/a = 1.568$ )	0.223	Potassium	bcc	0.461
Cadmium	cph ( $c/a = 1.886$ )	0.298	Rhodium	fcc	0.269
Chromium	bcc	0.250	Rubidium	bcc	0.494
Cobalt	cph ( $c/a = 1.623$ )	0.250	Silver	fcc	0.289
Copper	fcc	0.255	Sodium	bcc	0.372
Gold	fcc	0.288	Tantalum	bcc	0.286
Iron	bcc	0.248	Thorium	fcc	0.360
Lead	fcc	0.350	Titanium	cph ( $c/a = 1.587$ )	0.299
Lithium	bcc	0.331	Tungsten	bcc	0.274
Magnesium	cph ( $c/a = 1.623$ )	0.320	Uranium	orthorhombic	0.275
Molybdenum	bcc	0.275	Vanadium	bcc	0.262
Nickel	fcc	0.249	Zinc	cph ( $c/a = 1.856$ )	0.266
Niobium	bcc	0.286	Zirconium	cph ( $c/a = 1.592$ )	0.318

### Diamond and Graphite

It is remarkable that a single element, carbon, can exist in two such different crystalline forms as diamond and graphite. Diamond is transparent and one of the hardest materials known, finding wide use, notably as an abrasive and cutting medium. Graphite finds general use as a solid lubricant and writing medium (pencil 'lead'). It is now often classed as a highly refractory ceramic because of its strength at high temperatures and excellent resistance to thermal shock.

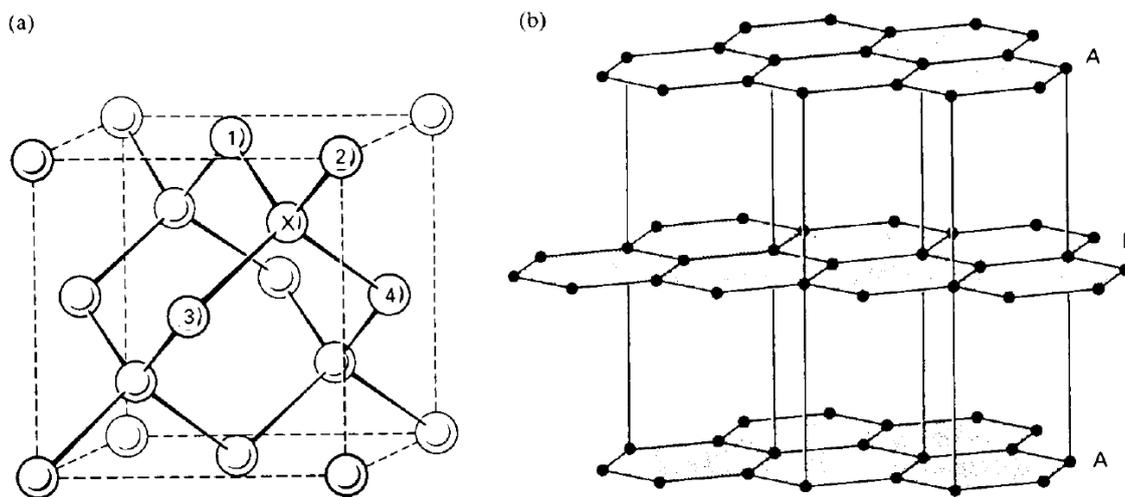


Fig. 17. Two crystalline forms of carbon: (a) diamond and (b) graphite

### Coordination in ionic crystals

We have seen in the case of diamond how the joining of four carbon atoms outlines a tetrahedron which is smaller than the structure cell. Before examining some selected ionic compounds, it is necessary to develop this aspect of coordination more fully. This approach to structure-building concerns packing and is essentially a geometrical exercise. It is subordinate to the more dominant demands of covalent bonding.

In the first of a set of conditional rules, assembled by Pauling, the relative radii of cation ( $r$ ) and anion ( $R$ ) are compared. When electrons are stripped from the outer valence shell during ionization, the remaining electrons are more strongly attracted to the nucleus; consequently, cations are usually smaller than anions.

Table 3: Relation between radius ratio and coordination

$r/R$	Maximum coordination number (CN)	Form of coordination
$<0.155$	2	Linear
$0.155-0.225$	3	Equilateral triangle
$0.225-0.414$	4	Regular tetrahedron
$0.414-0.732$	6	Regular octahedron
$0.732-1.0$	8	Cube
$1.00$	12	Cuboctahedron

## AB type compound

MgO is a sodium chloride-type structure, with  $\text{Mg}^{2+}$  cations and  $\text{O}^{2-}$  anions occupying two interpenetrating fcc sub-lattices. Many oxides and halides have this type of structure (e.g. CaO, SrO, BaO, VO, CdO, MnO, FeO, CoO, NiO; NaCl, NaBr, NaI, NaF, KCl, etc.). The ratio of ionic radii  $r/R = 0.065/0.140 = 0.46$  and, each  $\text{Mg}^{2+}$  cation is octahedrally coordinated with six larger  $\text{O}^{2-}$  anions, and vice versa (CN = 6:6). Octahedra of a given type share edges. The 'molecular' formula MgO indicates that there is an exact stoichiometric balance between the numbers of cations and anions; more specifically, the unit cell depicted contains  $(8 \times 1/8) + (6 \times 1/2) = 4$  cations and  $(12 \times 1/4) + 1 = 4$  anions.

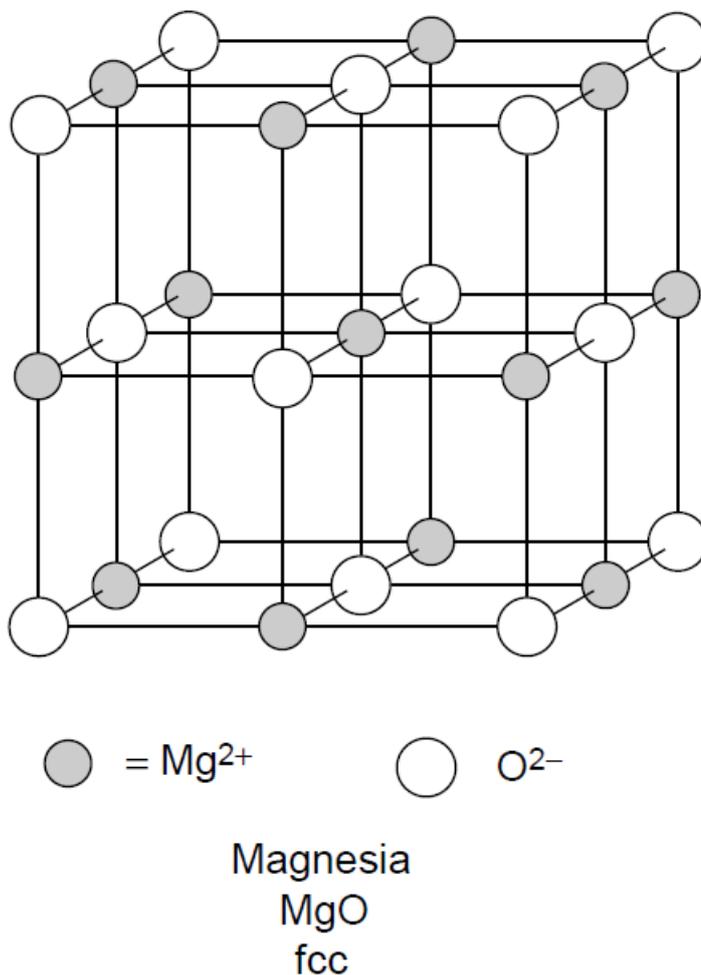


Fig 18. AB-type compounds

## Silica

Compounds of the  $\text{AB}_2$ -type (stoichiometric ratio 1:2) form a very large group comprising many different types of structure. We will concentrate upon  $\beta$ -cristobalite, is the high temperature modification of one of the three principal forms in which silica ( $\text{SiO}_2$ ) exists. Silica is a refractory ceramic which is widely used in the steel and glass industries. Silica bricks are prepared by kiln-firing quartz of low impurity content at a temperature of  $1450^\circ\text{C}$ , thereby

converting at least 98.5% of it into a mixture of the more ‘open’, less dense forms, tridymite and cristobalite.

Table 4: Principal crystalline forms of silica

<i>Form</i>	<i>Range of stability (°C)</i>	<i>Modifications</i>	<i>Density (kg m<sup>-3</sup>)</i>
Cristobalite	1470–1723 (m.p.)	$\beta$ —(cubic)	2210
		$\alpha$ —(tetragonal)	2330
Tridymite	870–1470	$\gamma$ —(?)	—
		$\beta$ —(hexagonal)	2300
		$\alpha$ —(orthorhombic)	2270
Quartz	<870	$\beta$ —(hexagonal)	2600
		$\alpha$ —(trigonal)	2650

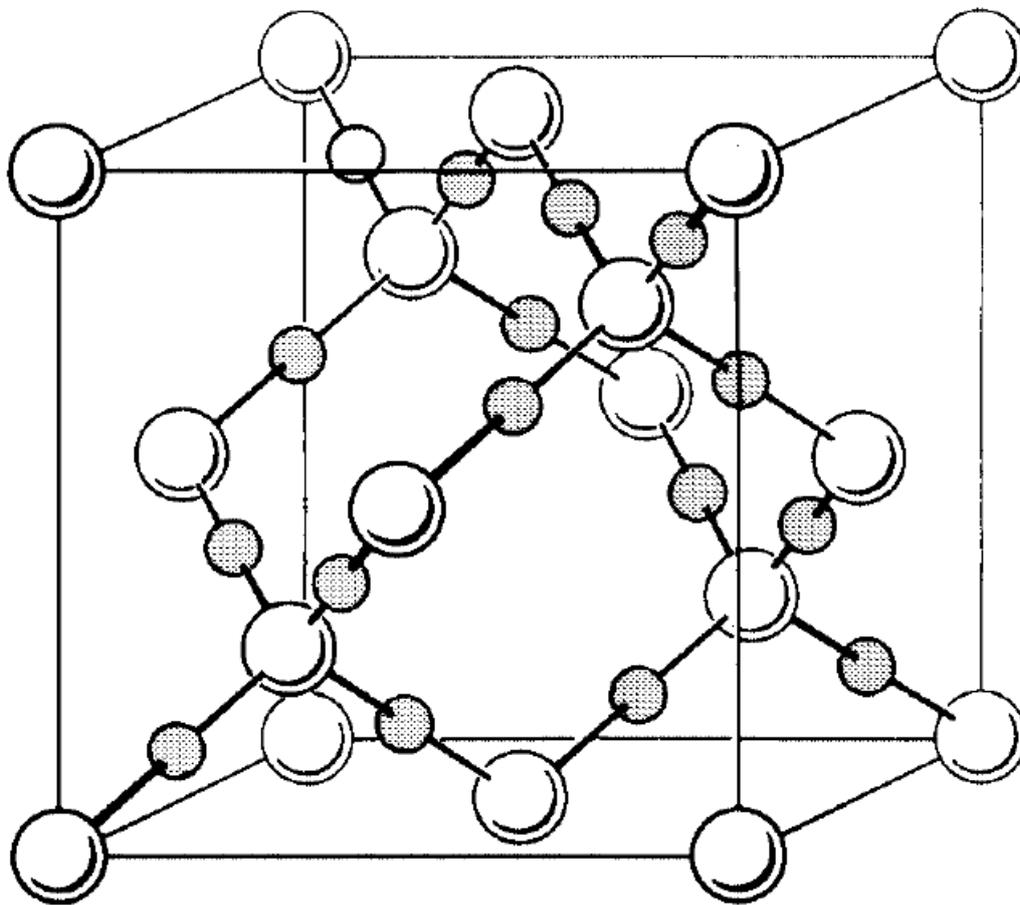
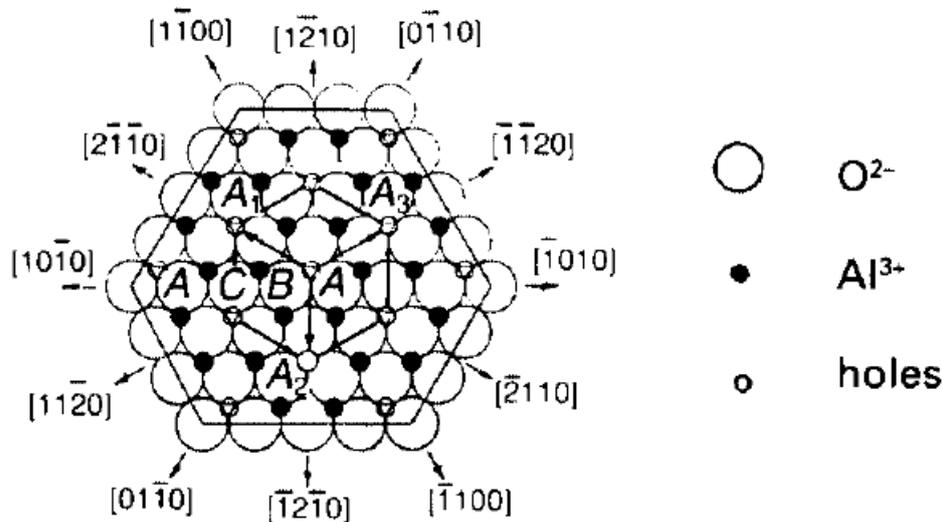


Fig 19. Structure of  $\beta$ -cristobalite

## Alumina

Alumina exists in two forms:  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$ . The former, often referred to by its mineral name corundum, serves as a prototype for other ionic oxides, such as  $\alpha$ - $\text{Fe}_2\text{O}_3$  (haematite),  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ ,  $\text{Ti}_2\text{O}_3$ , etc.

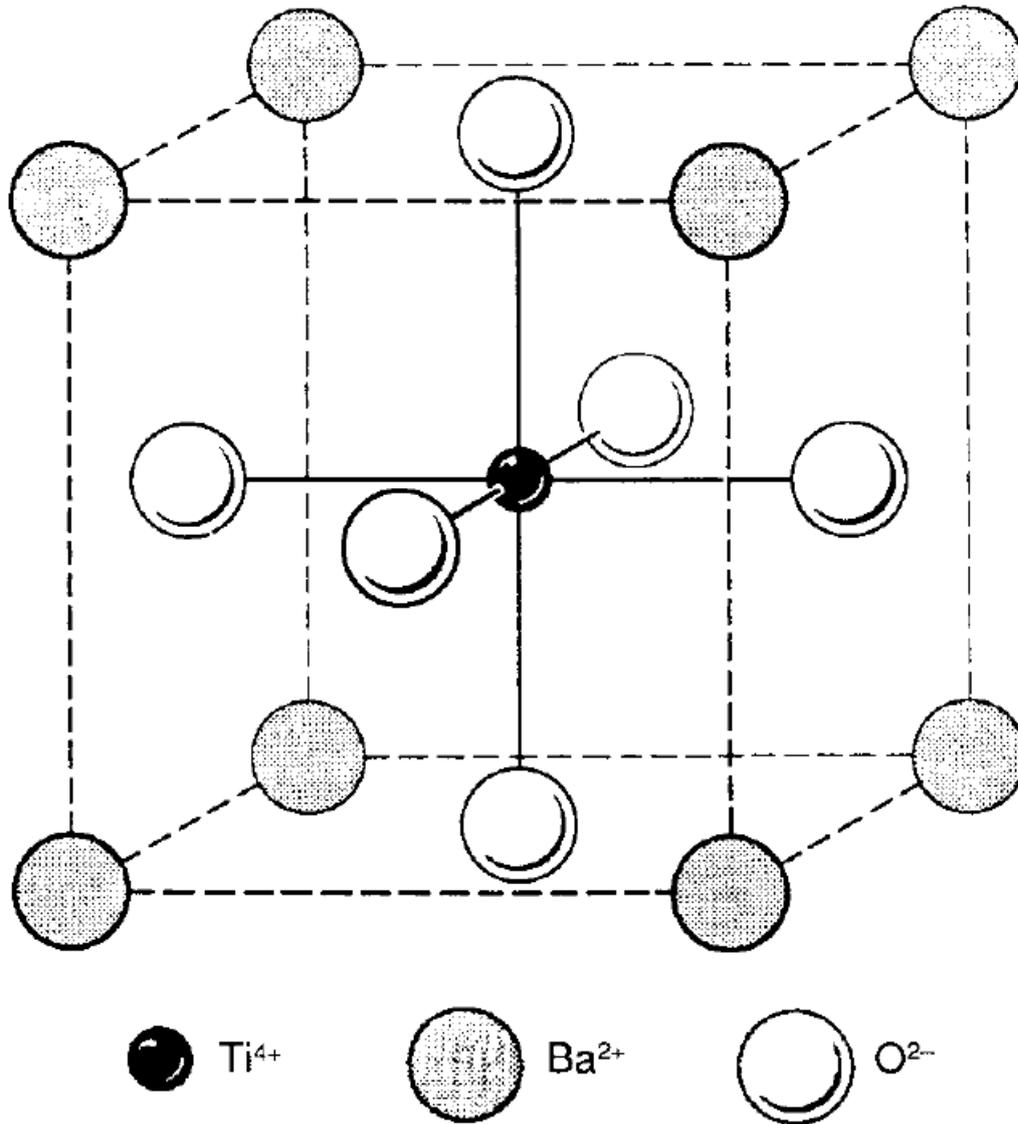


**Figure 20** Structure of  $\alpha$ -alumina

$\gamma$ - $\text{Al}_2\text{O}_3$  has very useful adsorptive and catalytic properties and is sometimes referred to as 'activated alumina', illustrating yet again the way in which structural differences within the same compound can produce very different properties.

## Complex oxides

The  $\text{ABO}_3$ -type compounds, for which the mineral perovskite ( $\text{CaTiO}_3$ ) is usually quoted as prototype, form an interesting and extremely versatile family. Barium titanium oxide ( $\text{BaTiO}_3$ ) has been studied extensively, leading to the development of important synthetic compounds, notably the new generation of ceramic superconductors. It is polymorphic exhibiting at least four temperature-dependent transitions. The cubic form, which is stable at temperatures below  $120^\circ\text{C}$ . Above the ferroelectric Curie point ( $120^\circ\text{C}$ ), the cubic unit cell of  $\text{BaTiO}_3$  becomes tetragonal as  $\text{Ti}^{4+}$  cations and  $\text{O}^{2-}$  anions move in opposite directions parallel to an axis of symmetry.

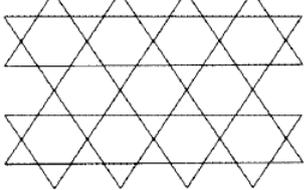


**Figure 21.** Unit cell of cubic  $\text{BaTiO}_3$  (CN = 6 :12)

### Silicates

Silicate minerals are the predominant minerals in the earth's crust, silicon and oxygen being the most abundant chemical elements. They exhibit a remarkable diversity of properties. Early attempts to classify them in terms of bulk chemical analysis and concepts of acidity/basicity failed to provide an effective and convincing frame of reference. An emphasis upon stoichiometry led to the practice of representing silicates by formulae stating the thermodynamic components. Thus two silicates which are encountered in refractories science, forsterite and mullite, are sometimes represented by the 'molecular' formulae  $2\text{MgO} \cdot \text{SiO}_2$  and  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . (A further step, often adopted in phase diagram studies, is to codify them as  $\text{M}_2\text{S}$  and  $\text{A}_3\text{S}_2$ , respectively.) However, as will be shown, the summated counterparts of the above formulae, namely  $\text{Mg}_2\text{SiO}_4$  and  $\text{Al}_6\text{Si}_2\text{O}_{13}$ , provide some indication of ionic grouping and silicate type. In keeping with this emphasis upon structure, the characterization of ceramics usually centres upon techniques such as X-ray diffraction analysis, with chemical analyses making a complementary, albeit essential, contribution.

**Table 5: Classification of silicate structures**

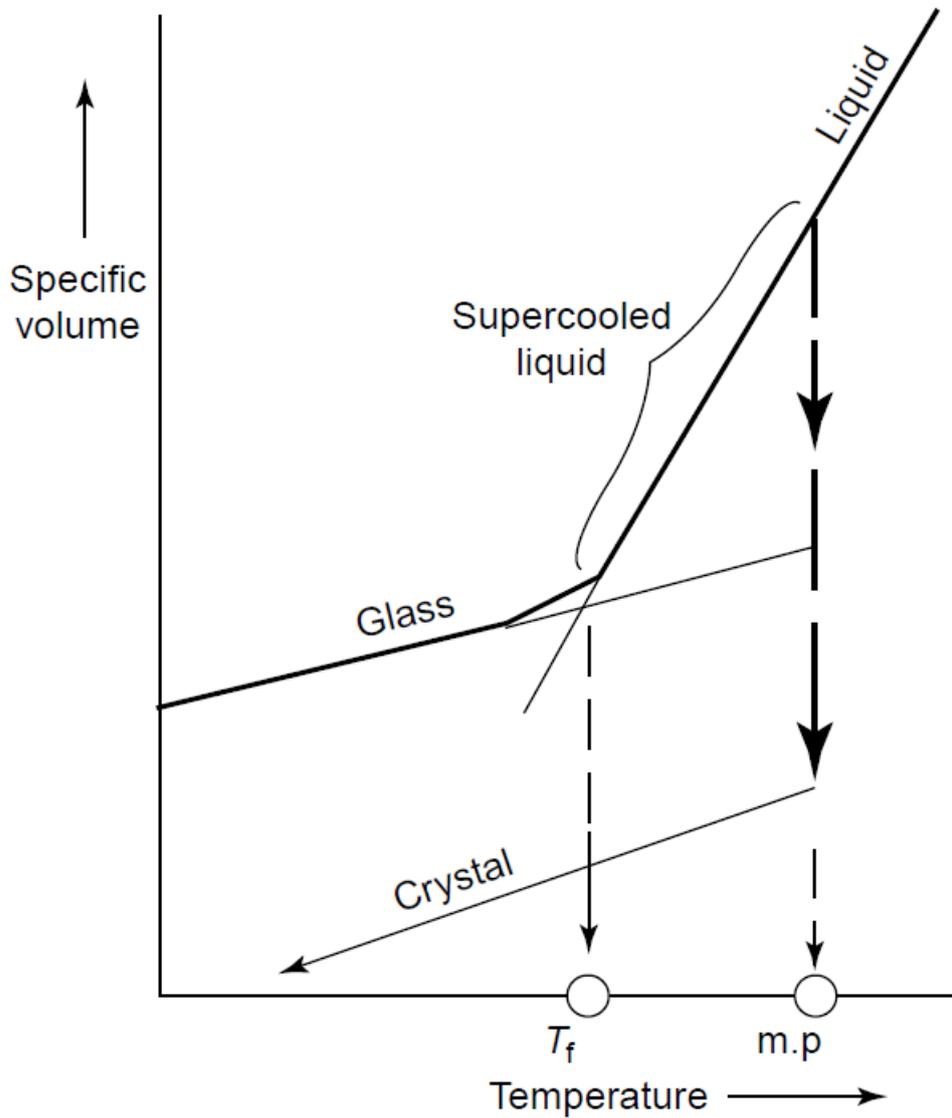
Type of silicate		$(Si^{4+} + Al^{3+}) : O^{2-}$ <sup>a</sup>	Arrangement of tetrahedra <sup>b</sup>	Examples
Mineralogical name	Chemical name			
Nesosilicate	'Orthosilicate'	1:4	Isolated 	Zircon, olivines, garnets
Sorosilicate	'Pyrosilicate'	2:7	Pairing 	Thortveitite
		1:3, 4:11	Linear chains 	Amphiboles, pyroxenes
Inosilicate	'Metasilicate'	3:9, 6:18, etc.		Beryl
			Rings 	
Phyllosilicate		2:5	Flat sheets 	Micas, kaolin, talc
				
Tectosilicate		1:2	Framework 	Feldspars, zeolites, ultramarines

<sup>a</sup>Only includes Al cations within tetrahedra.

<sup>b</sup>Δ represents a tetrahedron.

### Network structures in glasses

Having examined a selection of important crystalline structures, we now turn to the less-ordered glassy structures. Boric oxide ( $B_2O_3$ ; m.p.  $460^\circ C$ ) is one of the relatively limited number of oxides that can exist in either a crystalline or a glassy state. Apart from chemical composition, the main variable controlling glass formation from oxides is the rate of cooling from the molten or fused state. Slow cooling provides ample time for complete ordering of atoms and groups of atoms. Rapid cooling restricts this physical process and therefore favours glass formation. Glasses do not cleave, because there are no crystallographic planes, and fracture to produce new surfaces that are smooth and shell-like (conchoidal). It is usually impossible to represent a glass by a stoichiometric formula. Being essentially metastable, the structure of a glass can change with the passage of time. Raising the temperature increases ionic mobility and hastens this process, being sometimes capable of inducing the nucleation and growth of crystalline regions within the glassy matrix. Controlled devitrification of special glasses produces the heat- and fracture-resistant materials known as glass ceramics.



**Figure 22.** Comparison of the formation of glass and crystals from a melt.

### References

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2. William D. Callister, Jr., David G. Rethwisch, "Materials Science and Engineering An Introduction", Eight Edition, John Wiley & Sons, Inc